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(54) Invention

Semiconductor Device and its manufacture

(57) Abstract

Purpose: To provide a semiconductor device and its manufacturing method capable of avoiding the decomposition of a reflection preventive film having stoichiometrically unstable bonds as well as forming a highly stable fine pattern.

Constitution: A reflection preventive film 12 having stoichiometrically unstable bonds is formed on an underneath substrate; a protective film 14 suppressing the change in the optical requirements of this reflection preventive film 12 is formed; and then a resist film is formed on this protective film 14 directly or through the intermediary of an interlayer film so as to be processed according to a specific pattern using photolithography.

#### Coverage of patent

Claim 1 – The manufacturing method of a semiconductor device which processes an underneath substrate. The underneath substrate has a resist film formed by a specific pattern using photolithography, and the resist film is used as a mask for etching. The manufacturing method includes the following processes: forming a reflection preventive film having stoichiometrically unstable bonds on the underneath substrate; forming a protective film suppressing the change in the film's optical requirements on the reflection preventive film; forming a resist film on this protective film directly or through the intermediary of an interlayer film; processing this resist film by a specific pattern using photolithography.

Claim 2 – The manufacturing method of the semiconductor device mentioned in the Claim 1 which is constituted by a reflection preventive film,  $\text{Si}_x\text{O}_y\text{N}_z$  (x is a real number that does not include 0, y is a real number that includes 0 and z is a real number that does not include 0).

Claim 3 – The manufacturing method of the semiconductor device mentioned in the Claim 1 and Claim 2 whose protective film is constituted by the same quality of the material with the optical characteristics as the interlayer film formed on the protective film.

Claim 4 - The manufacturing method of the semiconductor device mentioned in the Claim 1 through 3: its protective film is constituted by an inorganic film with refracting rate, n, is between 1.4 and 1.7 to wavelength for exposure light; its interlayer film is constituted by a silicon oxide film.

Claim 5 - The manufacturing method of the semiconductor device mentioned in the Claim 1 through 4 whose protective film is formed by the plasma TEOS method.

Claim 6 - The manufacturing method of the semiconductor device mentioned in the Claim 1 through 5 whose protective film is formed at the temperature below that of the reflection preventive film is formed.

Claim 7 - The manufacturing method of the semiconductor device mentioned in the Claim 1 through 6 whose protective film is an insulation film and also serves as an interlayer film.

Claim 8 – In a semiconductor device with a MOS transistor, a reflection preventive film is formed on a gate electrode of the MOS transistor. The reflection preventive film is constituted by  $\text{Si}_x\text{O}_y\text{N}_z$  (x is a real number that does not include 0, y is a real number that includes 0 and z is a real number that does not include 0). A protective film is formed over the reflection preventive film and suppresses the change in the optical requirements of this reflection preventive film. The semiconductor device whose protective film is at least a part of the offset oxide film of the gate electrode.

Claim 9 – A semiconductor device with lower wiring layers, interlayer insulation film and upper wiring layers. The lower wiring layers and the upper wiring layers are connecting each other through the contact hole formed in the interlayer insulation film. On the surface of the lower wiring layer, it is formed a reflection preventive film is formed, and it is constituted by  $\text{Si}_x\text{O}_y\text{N}_z$  (x is a real number that does not include 0, y is a real number that includes 0 and z is a real number that does not include 0). On this reflection preventive film, there is a protective film suppressing the change in the optical requirements of this reflection preventive film.

Claim 10 – The protective film mentioned above is formed by plasma TEOS method at the temperature below that of the reflection preventive film is formed. The semiconductor device mentioned in the Claim 8 contains such protective film.

Claim 11 – The protective is an interlayer insulation film, and is formed by the plasma TEOS method in the temperature below that of the reflection preventive film is formed. The semiconductor device mentioned in the Claim 9 has such film.

### **Explanation**

#### **0001 – Industrial use**

This invention is a semiconductor device as well as its production method. Furthermore, it is a semiconductor device that is capable of forming a stable fine pattern as well as its production method.

#### **0002 – Conventional technique**

For the research and development of semiconductor integrated circuit, a design rule device for the sub-half micron domain has been developed. The photolithography technique is used for the development of such devices, and a light exposure device called Stepper (a retrenchment projection exposure) whose light source exposure is a single wavelength is used in the photolithography.

0003 – When a single wavelength is used for exposure, a phenomenon known as “Standing Wave Effects” is noted. Multiplex interference of light exposure in the resist film causes the effects. As in the chart 1, the incident light P and the reflected light R in the interface between the resist PR and the substrate S intervene each other in the resist film. As a result, the amount of light being absorbed to the resist (y-axis) changes depending on the thickness of the resist film (x-axis) as shown in the chart 2. Now, the amount of light being absorbed to the resist means that the light being absorbed to the resist itself which excludes lights of the surface reflection on the resist surface or absorption in the substrate and emission from the resist. Such lights being absorbed to the resist become energy for light reaction.

0004 – The chart 2 shows the variation of the amount of lights being absorbed by the thickness of resist film (XP 8843) on a silicon substrate, assuming KrF is  $\lambda = 248\text{nm}$  as the light for the light exposure. For the true device, there is always unevenness on the substrate as shown in the chart 3. For example, there is always a convex In of poly silicon, so when the resist film PR is coated, the thickness of the film differs between top and bottom sides. That is, the thickness  $d_{prz}$  on the convex part In is thinner than that on the other sides.

0005 – Because the Standing Wave Effects depend on the thickness of the resist film (see above), the amount of the light being absorbed to the resist, which is influenced by the effect, changes. As a result, exposure and the size of the resist pattern after the phenomenon differs between top and bottom sides. The more the size of the resist pattern gets detailed, the clearer the Standing Wave Effects influences the pattern size. Every kind of resist has the same phenomenon.

0006 – Generally, the precision of the size of resist pattern in the process of photolithography is plus and minus 5 percent. It is necessary to reduce the Standing Wave Effects to achieve such precision. The chart 4 shows the size variations in the resist pattern (y-axis) to the amount variations in the light absorption in the resist film. The chart clearly shows that it is required to keep the amount variations in the light absorption within the range 6 percent to produce a device with the rule of 0.35 $\mu$ m.

0007 – issues that the invention tries to resolve

To meet the above requirement investigations of the techniques of reflection preventive film are carried out in the various fields. As a result, the inventor has discovered that Si C SiO<sub>x</sub>, Si<sub>x</sub>O<sub>y</sub>N<sub>z</sub>, Si<sub>x</sub>N<sub>y</sub> are superior materials for a reflection preventive film on a high melting point metal silicide (W-Si), metal (Al-Si) or silicon system materials (Poly-Si). They all need a reflection preventive film.

0008 – To produce a device, especially the one with 0.35 $\mu$ m design rule, it is necessary to use the Selfaline contact method (SAC). To use this method, an offset oxide film is formed on the gate electrode with W-Si, and a photoresist layer is formed on the oxide film. Then the semiconductor mask patterns are transcribed to the resist. The semiconductor device is produced by etching the offset oxide film and the high melting point metal silicide (W-Si) and silicon system material (Poly-Si) using the transcribed resist as a mask.

0009 – The inventor has discovered that it is effective to form a reflection preventive film, which is constituted by SiO<sub>x</sub>, Si<sub>x</sub>N<sub>y</sub>, Si<sub>x</sub>O<sub>y</sub>N<sub>z</sub> films, under the resist film when fine patterns are formed during the formation of semiconductor mask patterns on the high melting point metal silicide (W-Si) and silicon system materials (Poly-Si).

0010 – However, the SiO<sub>x</sub>, Si<sub>x</sub>N<sub>y</sub>, Si<sub>x</sub>O<sub>y</sub>N<sub>z</sub> films are not stoichiometrically stable. Therefore, when the offset oxide film is formed on these reflection preventive films and the fine patterns are formed over the films, the quality of the reflection preventive films changes if the filming temperature is high (changes in optical requirements). This reduces reflection preventive effects and makes it difficult to form a stable detailed pattern. So, it has been essential to deal with this issue.

0011 – The purpose of this invention is to provide a semiconductor device and its manufacturing method capable of avoiding the decomposition of the reflection preventive film having stoichiometrically unstable bonds as well as forming a highly stable fine pattern.

0012 – Means and actions to solve the issue

When a semiconductor device is produced using an i-beam (365 nm) or a short wavelength light (i.e. KrF, ArF Excimer laser) as a light source, this invention makes it possible to form a stable fine pattern. To do so, it is necessary to fix a protective film on a reflection preventive film in order to prevent decomposition of the reflection preventive film that has stoichiometrically unstable bonds. The protective film controls the variation of optical requirements and prevents decomposition of the reflection preventive film.

0013 – The following steps are used to fix the reflection preventive film:

(I) Get a contour line for light absorption amount in the resist film to thickness of a resist when the optical requirements, n and k, for the reflection preventive film changes continuously (the thickness of the reflection preventive film is fixed at will).

0014 – (II) Based on the results, find a common domain that the difference of the light absorption

amount becomes the smallest. The optical requirements in this domain become  $n$  and  $k$  which are fixed as the optical requirements for the film thickness of reflection preventive film, mentioned in (I).

0015 – (III) Repeat the operations (I) and (II) changing the thickness of the reflection preventive film and get the optical constants,  $n$  and  $k$ , for each condition. (IV) Find the reflection preventive film materials which have the optical constants obtained in the step (III).

0016 – Now the following is a concrete explanation of the above steps. 1) To get the intermediary of maximum value of the Standing Wave Effects or the intermediary of minimum value of resist thickness,  $\lambda/4n$  when refraction rate of resist is  $n_{pr}$  and a wavelength of the exposure light is  $\lambda$ . (refer chart 5)

0017 – 2) Process a reflection preventive film ARL between a resist and an underneath substrate with the thickness,  $d_{arl}$ , and optical constant,  $n_{arl}$  and  $k_{arl}$ . 3) Attention to some spot in the film thickness, for example, the thickness at the maximum the Standing Wave Effects. Changing  $n_{arl}$  and  $k_{arl}$  while fixing the thickness  $d_{arl}$ , the light absorption amounts of the resist film at each point change. The chart 6 shows a locus of this changes which is a contour line for light absorption amount in the resist film.

0018 – 4) For other different resist film thickness,  $d_{pr}$ , the charts 7 through 9 show the results corresponds to the chart 6, when the step 3 is conducted repeatedly to four different points with a space of  $\lambda/8 n_{pr}$ , based on the film thickness that makes the Standing Wave Effects at the maximum or at the minimum. The charts show the results when thickness for the reflection preventive film is fixed at 20 nm and thickness for each resist film is fixed at 985 nm, 1000 nm, 1018 nm and 1035 nm. The steps 1 through 4 apply to the procedure (I).

0019 – 5) The common domain in the charts 6 through 9 show the area that the light absorption amount does not change in the resist film even though the thickness of the resist film changes. This means that the common domain is the area that makes the Standing Wave Effects as minimum as possible and is highly effective for the reflection prevention. Therefore, it is essential to find the common domain. To get the common domain easily, place one chart upon another or search for it by computer. This step applies to the procedure (II).

0020 – 6) Now, changing the thickness for reflection preventive film,  $d$ , conduct 3, 4 and 5 repeatedly. For example, the steps 3, 4 and 5 are conducted with  $d=20$  nm and then change  $d$ 's figure and repeat these steps again. By doing so, it is possible to specify the requirements of reflection preventive film,  $d_{arl}$ , optical constant  $n_{arl}$  and  $k_{arl}$  that keeps the Standing Wave Effects as minimum as possible. This applies to the procedure (III).

0021 – 7) It is possible to find a film that meets the requirements of thickness and the optical constant being specified in the step 6 by measuring the optical constant in the light exposure for each type of film. This applies to the procedure (IV). In principle, this step is applicable for every wavelength and all underneath substrates.

0022 – Using the procedures I through IV, the following materials are appropriate for the reflection preventive films in this invention: silicon system films such as single crystallization silicon, multi-crystallization silicon, amorphous silicon, doped poly silicon. Also, it is appropriate to use the  $Si_xO_yN_z$  film as the reflection preventive film on the highly reflective substrate such as high melting point metal silicide system films.

0023 – For silicon system films or reflection preventive films on a highly reflective substrate, it is desirable to use inorganic film whose optical constant is:  $n=1.7\sim2.4$ ,  $k<0.90$  (possibly  $0.1<k<0.6$ ), such as the  $\text{Si}_x\text{O}_y\text{N}_z$  film (it is okay to contain hydrogen H) or the  $\text{Si}_x\text{N}_y$  film with thickness of 20~300 nm.

0024 – For example, a  $\text{Si}_x\text{O}_y\text{N}_z$  film or a  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film is able to control an imaginary number of refraction rate k depending on the condition at forming the film. i.e. in a wavelength belt of 248 nm and the actual number of refraction rate n of 2.8, the film can control an imaginary number of refraction rate k by changing the flow rate of silane-base gas. Therefore, a reflection preventive film for a specific substrate with certain optical constant can be made easily.

0025 – For example, it is appropriate to use a reflection preventive film with  $n=2.12$ ,  $k=0.54$  and  $d=29$  nm for the W-Si substrate to keep the Standing Wave Effects as minimum as possible. For Al-Si substrate, it is appropriate to use a reflection preventive film with  $n=2.09$ ,  $k=0.87$  and  $d=24$  nm to to keep the Standing Wave Effects as minimum as possible. For the Si substrate, it is appropriate to use a reflection preventive film with  $n=2.0$ ,  $k=0.55$  and  $d=32$  nm to keep the Standing Wave Effects as minimum as possible.

0026 – The charts 11, 12 and 13 show the comparison of the Standing Wave Effects with and without a  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film being formed on the tungsten silicide, aluminum silicon and single crystallization silicon separately. As in the charts, using the a  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film with the appropriate condition as a reflection preventive film, it is possible to minimize the Standing Wave Effects, and to achieve the reflection preventive effect.

0027 – However, the a  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film is stoichiometrically unstable film despite the advantage that the optical constant can be set freely. The chart 14 shows the FT-IR spectroscopic analysis. The bonding condition of a  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film with the anile process at the temperature over 500C is different from it is immediately after the formation. As the film's bonding condition changes, its optical requirements change which may not keep the good reflection preventive effect.

0028 – Now, to protect a stoichiometrically unstable reflection preventive film, one of the possible ways is to form a protective film on the reflection preventive film. Nevertheless, not all protective films are applicable because the special quality of the reflection preventive film should not change by heat treatment at the formation of the protective film.

0029 – The inventor has found that to protect bonding condition of the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film, a stoichiometrically stable film should be formed as protective film on the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film with the same formation temperature of the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film.

0030 – For an intermediary of an interlayer film with self align contact technique, an oxide film with thickness of 80-200 nm is used. The real number of the film's optical constant is about  $n=1.4\sim1.7$ . Therefore, it is possible to prevent decomposition of the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film. For example, a silicon oxide film with thickness 30nm is formed on the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film by P-TEOS method with the same forming device and temperature, and then form a silicon oxide film with thickness of 140nm as an intermediary of an interlayer film by LP-TEOS method at 720 C. Because forming a silicon oxide film by the P-TEOS method and by the LP-TEOS method is optically the same, the reflection preventive effect of the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film is not disappear.

0031 – This means that a stable pattern can be formed by using a protective film to prevent decomposition of a reflection preventive film that contains stoichiometrically unstable bonds. Meeting the above objective, the invention has completed. To do so, the manufacturing method of this semiconductor device includes the following processes: formation of a reflection preventive film that contains stoichiometrically unstable bonds on an underneath substrate; formation of a protective film on the reflection preventive film to prevent decomposition of optical requirements for the reflection preventive film; formation of a resist film directly or through the intermediary of an interlayer film on the protective film; and processing the resist film to a designated pattern by photolithography method.

0032 – It is preferable for the reflection preventive film to be constituted with the  $\text{Si}_x\text{O}_y\text{N}_z$  (x is a real number excluding 0, y is a real number including 0 and Z is a real number excluding 0). A  $\text{Si}_x\text{O}_y\text{N}_z$  film or a  $\text{Si}_x\text{N}_y$  film as a reflection preventive film can be formed easily by CVD method with gas system including silicon. For example, using parallel flat style plasma CVD method, ECR plasma CVD method, or bias ECR plasma CVD method, it is possible to form such films by micro wave and mixed gas,  $\text{SiH}_4 + \text{O}_2 + \text{N}_2$  or  $\text{SiH}_4 + \text{N}_2\text{O}$ . The Algon Ar gas can be used as buffer gas.

0033 – The reflection preventive film,  $\text{Si}_x\text{O}_y\text{N}_z$  film or  $\text{Si}_x\text{N}_y$  film, can etch easily by RIE. The RIE contains enhanced ionic nature by making a resist as a mask and  $\text{CF}_4$ ,  $\text{CHF}_3$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_4\text{F}_6$ ,  $\text{SF}_6$ ,  $\text{S}_2\text{F}_2$ ,  $\text{NF}_3$  gas as enchanters and adding Ar. It is desirable to conduct RIE under the pressure of 2 Pa with the power of 10-100 W. Also, the gas flow at the RIE is preferred to be set between 5 and 70SCCM.

0034 – The materials of the protective film are desirable to have the same optical characteristics as an interlayer film. It is better to be constituted by inorganic materials. The preferred thickness is between 20 and 200 nm. The protective film is desirable to be constituted by an inorganic film with refracting rate (n) is between 1.4 and 1.7, and the interlayer film is desired to be constituted by a silicon oxide film.

0035 – The protective film is desirable to be made by plasma TEOS method or ozone TEOS method. It is desirable that the protective film is formed at the temperature below the one that forms the reflection protective film. In details, it is desirable that the protective film is formed below 500 C.

0036 – It is desirable to use the same formation device when a reflection protective film and a protective film are formed or the reflection protective film, the protective film and the interlayer film are formed. The protective film is an insulation film and can be interlayer film at the same time. To do so, the first semiconductor device has a reflection preventive film constituting the  $\text{Si}_x\text{O}_y\text{N}_z$  (x is a real number excluding 0, y is a real number including 0 and Z is a real number excluding 0) is formed on a gate electrode in the MOS transistor. And, the protective film is formed on the reflection preventive film to protect the optical requirements of the film from the decomposition and is a part of the offset oxide film in the gate electrode.

0037 – The second semiconductor device has lower wiring layers, an interlayer insulation film and upper wiring layers. The lower wiring layers and the upper wiring layers are connected through the contact hole formed in the interlayer insulation film. A reflection preventive film which is constituted by the  $\text{Si}_x\text{O}_y\text{N}_z$  (x is a real number excluding 0, y is a real number including 0 and Z is a real number excluding 0) is formed on the surface of the lower wiring layer. An interlayer insulation film with a function to prevent the decomposition of the optical requirements of the reflection preventive film is formed on the reflection preventive film.

### 0038 – Utilization

The following are examples of utilization. The invention is, of course, not limited to following examples.

### 0039 – Example 1

This is an example of utilization of this invention at the formation of stable mask pattern on a high reflection substrate by using a protective film. Using i-laser, KrF, or ArF Excimer laser as a light source for this device, when semiconductor mask pattern is formed on a high reflection substrate, a protective film is used to prevent decomposition of a reflection preventive film which has stoichiometrically unstable bonds.

0040 – The chart 15 shows the manufacturing method of the semiconductor device. For example, the method is appropriate for the production process of a gate electrode with high melting point metal silicide such as W or W-Si. However, it is also applicable to other kinds of substrates, resists and high reflection layers.

0041 – The chart 15 shows the manufacturing process of the semiconductor device. The gate electrodes for the NMOS transistor the PMOS transistor are formed on a semiconductor substrate 2.

0042 – A silicon wafer is used for the semiconductor substrate 2. An element isolation region 4 is formed on surface of the semiconductor substrate 2. This is formed by some methods such as LOCOS method or Trench style element isolation method. After the element isolation region 4 is formed on the substrate's surface, a gate insulation film 6 is formed on the surface of the semiconductor substrate 2. The film is formed by heat oxidation of the surface of the semiconductor substrate 2 and is constituted by silicon oxidant.

0043 – Next, a poly silicon film 8 is formed on the surface of the gate insulation film. A tungsten silicide film 10 is formed by CVD method on the surface of the poly silicon film 8. Both the poly silicon film 8 and the tungsten silicide film 10 become gate electrode for the MOS transistor. The following is a method of patterning process.

0044 – First of all, a reflection protective film 12 is formed to process both the poly silicon film 8 and the tungsten silicide film 10 to fine patterns. A  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film with its optical constant,  $n=1.7-2.4$  and  $k<0.9$  (preferably  $0.1 < k < 0.6$ ) and its thickness of 20-300nm is used as a reflection protective film 12.

0045 – The  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film can be formed easily by each CVD method including silicon gas system. For example, the film is used one of the methods such as parallel flat plasma CVD, ECR plasma CVD, or Bias ECR plasma CVD. Using micro wave and mixed gas (i.e.  $\text{SiH}_4 + \text{O}_2 + \text{N}_2$  or  $\text{SiH}_4 + \text{N}_2\text{O}$ ) the film can be formed. In this process, argon (Ar) gas can be used as buffer gas. The temperature is around 350-400 C for example.

0046 – Next, a protective film 14 is formed on the reflection protective film 12. The protective film 14 also works as offset oxide film. Its thickness is 20-200 nm. The protective film is a film to prevent the decomposition of the optical requirements of the reflection preventive film 12 that is constituted by stoichiometrically unstable  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film. The protective film is constituted by silicon oxide films which are formed by several methods such as CVD method at temperature below 500 C, plasma TEOS method or ozone TEOS method. It is possible to use the same device to form the reflection protective film 12 and the protective film 14.

0047 – Then, a resist film is formed on the protective film including an offset oxidant film by spin coating method, and the photo lithography process is conducted on the resist film. The exposure light for the photo lithography is i-laser with 365 nm or longer wave length light such as i-laser, KrF, ArF Excimer laser.

0048 – The reflection preventive film 12 keeps the Standing Wave Effects as minimum as possible and makes it possible to form an extremely precise and fine pattern. The Standing Wave Effects is caused by existence of a highly reflective tungsten silicide film on the lower layer of the resist film. The optical requirements for the reflection protective film are set in the optimum to prevent the Standing Wave Effects. Because the protective film 14 prevents the decomposition of the optical requirements, it is possible to form a stable fine pattern in the resist film.

0049 – After that, making the resist film as a mask, the protective film 14, the reflection preventive film 12, the tungsten silicide film 10 and the poly silicon film 8 go through the etching process. The chart 15 shows the process. The  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film as the reflection preventive film 12 can be easily etched by RIE. The RIE contains enhanced ionic nature by making a resist as a mask and  $\text{CF}_4$ ,  $\text{CHF}_3$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_4\text{F}_6$ ,  $\text{SF}_6$ ,  $\text{S}_2\text{F}_2$ ,  $\text{NF}_3$  gas as enchantants.

0050 – In order to form a source drain domain with LDD constitution, a low concentrated impurities diffusion layer 16 is formed by injecting ion into both the NMOS transistor domain and the PMOS transistor domain. Then, making the protective film 14 as the offset oxide film, and an insulated side walls are formed on both sides of the film. The source drain domain with LDD constitution is formed by injecting ion from the top of the side walls. After that, the semiconductor device is made following the normal SRAM manufacturing process.

0051 – When the semiconductor device is made by using i-laser of 365 nm or longer wave length light such as i-laser, KrF, ArF Excimer laser, it is possible to form a stable fine pattern even though the reflection protective film 12 has stoichiometrically unstable bonds. This is because a protective film is used on the reflection preventive film and the protective film prevents deterioration of the quality of the reflection preventive film. It is also used as the offset oxide film so the manufacturing process remains unchanged.

0052 – The following experiment proves that the protective film 14 is capable of preventing the decomposition of the optical requirements of the reflection preventive film that has stoichiometrically unstable bonds. As in the chart 16, a  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film 20 is formed on the tungsten substrate 18. The film is formed by the bias ECR plasma CVD method using micro wave (2.45 GHz), mixed gas of  $\text{SiH}_4 + \text{O}_2 + \text{N}_2$  and Ar as buffer gas. The temperature at the formation is 360 C and the thickness of the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film is 30 nm.

0053 – With the same film formation device, a silicon oxide film 22 is formed on the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film by the CVD method at the temperature 420 C. The thickness of the film is 170 nm. The table 1 shows the constitutions of this multi layered film measured by the SOPRA's ELLI system.

0054 - Table 1

	Density	Thickness (mm)
Silicon oxide film 22	-0.022 (void)	170.5
Intermediary layer film 24	-1.19 (silicon oxide)	0.00
$\text{Si}_x\text{O}_y\text{N}_z : \text{H}$ film 20	-0.060 (void)	30.3

0055 – The density in the table 1 means the ratio of void in the silicon oxide film 22 and the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film, and the ratio of silicon oxide in the interlayer film 24. The smaller the figure is the finer the film is. The intermediary layer film 24 is an intermixed film that is formed on the interface between the silicon oxide film 22 and the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film. The thickness is measured after the formation of the multi layered film.

0056 – As table 1 shows, when the silicon oxide 22 is formed on the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film 20 according to the above conditions, the intermediary layer film 24 is barely formed and the quality and the optical requirements of the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film 20 remain unchanged.

0057 – To the contrary, the same experiment is conducted except forming the silicon oxide film 22 with the LP-TEOS method at 720 C. The results shows in the table 2.

0058 – Table 2

	Density	Thickness (mm)
Silicon oxide film 22	0.054 (void)	177.2
Intermediary layer film 24	0.488 (silicon oxide)	32.2
$\text{Si}_x\text{O}_y\text{N}_z : \text{H}$ film 20	-53.8 (void)	0.4

0059 – As table 2 shows, when the silicon oxide 22 is formed by the LP-TEOS method at 720 C, the intermediary layer film 24, an intermixed film, is formed with the thickness of 32.2 nm. The quality of the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film 20 changes greatly with the decomposition of its optical requirements.

0060 – The above result is expected from the analysis of the FT-IR spectrum shown in the chart 14. It is desired to form a protective film on the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film 20 as reflection protective film under 500 C.

Example 2 – As the chart 17 and 18 show, this invention applies to the wiring constitution that the first wiring layer 30 connects with the second wiring layer 32 through contact hole 34.

0061 – As shown in the chart 17, the first wiring layer 30 is formed on the interlayer insulation film 36. The first wiring layer 30 is tungsten silicide. A reflection protective film 38 is formed on the first wiring layer 30.

0062 - An  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film is used for the reflection protective film 38. Its optical constants are  $n=1.7-2.4$ ,  $k<0.90$  (preferably  $0.1 < k < 0.6$ ) and the thickness is 20-300 nm. The film can be made easily by several CVD methods using silicon system gas. For example, this film is used parallel flat style plasma CVD method or ECR plasma CVD method or bias ECR plasma CVD method. It is also used micro wave and mixed gas,  $\text{SiH}_4 + \text{O}_2 + \text{N}_2$  or  $\text{SiH}_4 + \text{N}_2\text{O}$ . Argon gas is used as buffer gas in this process. The temperature at the formation of the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film is 350-400 C.

0063 – Then, a protective film 40 is formed on the reflection preventive film 38. The thickness of the protective film 40 is around 20-200 nm. Because an interlayer film 42 is formed on the protective film 40, it is okay to form a protective film 40 with the thickness of 20-50 nm. The protective film 40 is a film that is to prevent decomposition of the optical requirements of the reflection preventive film that is constituted by the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film having stoichiometrically unstable bonds. The protective film 40 is constituted by the silicon oxide film which is formed at below 500 C by the CVD method and the silicon oxide film which is formed by either plasma TEOS method or

ozone TEOS method. It is possible to form the reflection protective film 38 and the protective film 40 with the same device.

0064 – Next, with the spin coating method a resist film is formed on the protective film 40, and photolithography process is done to the resist film. The exposure light for the photolithography is i-laser of 365 nm or longer wave length light such as i-laser, KrF, ArF Excimer laser.

0065 – The Standing Wave Effects occur because the first wiring layer 30, which is constituted by a highly reflective tungsten silicide film, exists on the lower part of the resist film. The reflection protective film 38 keeps the Standing Wave Effects as minimum as possible and makes a precise and fine pattern. The optical requirements of the reflection protective film set appropriately to keep the Standing Wave Effects as minimum as possible. The protective film 40 prevents the decomposition of the optical requirements. Therefore, it is possible to form a fine pattern to the resist film.

0066 – The first wiring layer 30 with the designated fine pattern is made after the etching process of the protective film 40, the reflection preventive film 38 and the conductive layer. Then the second interlayer insulation film 42 is formed on the first interlayer insulation film 36 and the protective film 40. It is desired that the second interlayer insulation film 42 is an inorganic film which has the same optical constant as the protective film 40. The second interlayer insulation film 42 is constituted by a silicon oxide film which is formed by the LP-TEOS method. The thickness of the film is between 80 and 200 nm.

0067 – Next, with the spin coating method, a resist film 44 is formed on the second interlayer insulation film 42 and process photolithography. The exposure light for the photolithography is i-laser of 365 nm or longer wave length light such as i-laser, KrF, ArF Excimer laser.

0068 – The reflection protective film 38 keeps the Standing Wave Effects as minimum as possible and makes a precise and fine pattern 46. The effect occurs because the first wiring layer 30, which is constituted by highly reflective tungsten silicide, exists in the lower side of the resist film 44. The optical requirements of the reflection protective film 38 are set appropriately to keep the effects as minimum as possible. Because the protective film 40 prevents the decomposition of the requirements, even though the second interlayer insulation film 42 is formed at over 500 C, it is possible to form a stable fine pattern to the resist film 44.

0069 – Then the second interlayer insulation film 42, the protective film 40 and the reflection preventive film 38 go through the etching process making the resist film 44 as a mask, and the contact hole 34 with a fine pattern is formed precisely (chart 18). Then the second wiring layer 32 is formed surrounding the contact hole 34, and it connects with the first wiring layer 30.

0070 – This example shows that it is possible to form a stable fine pattern by using the protective film 40 even if the reflection preventive film 38 having stoichiometrically unstable bonds is used for manufacturing a semiconductor device. The protective film 40 should prevent the decomposition of the quality of the reflection film 38. When the semiconductor device is manufactured, an i-laser of 365 nm or a longer wave length light such as i-laser, KrF, ArF Excimer laser is used as a light source.

0071 – Also, by using the protective film 40 it is possible to prevent the decomposition of the optical requirements of the reflection preventive film 38 which has stoichiometrically unstable bonds even if the interlayer insulation film 42 is formed at over 500 C. The following experiment proves this possibility.

0072 – An  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film 50 is formed on the tungsten silicide substrate 48 as the reflection preventive film. The film 50 is formed by the bias ECR plasma CVD method. Micro wave (2.45 GHz) and mixed gas,  $\text{SiH}_4 + \text{O}_2 + \text{N}_2$  with Ar as buffer gas are used to form the film. The temperature to form the film is 360 C and the thickness of the film is 30 nm.

0073 – With the same forming device and the same forming temperature, a P-TEOS silicon oxide film 52 is formed by the plasma TEOS method on the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film 50 as a protective film. The thickness of the film is 30 nm. Then as an interlayer insulation film, a LP-TEOS silicon oxide film 54 is formed by the LP-TEOS method at 720 C. The thickness of the film is 140 nm.

0074 – The following is the measurement of the constitutions of a multi-layered film using SOPRA's ELLI system.

0075 – Table 3

	Density	Thickness (mm)
TEOS Silicon oxide film 54	-0.022 (void)	140
P-TEOS Silicon oxide film 52	-0.001 (void)	30
Intermediary fil 56	-0.005 (P-TEOS)	0.1
$\text{Si}_x\text{O}_y\text{N}_z : \text{H}$ film 50	0.003 (void)	31.0

0076 – The density in the table 3 means the ratio of void in the TEOS silicon oxide film 54, the P-TEOS silicon oxide film 52, or the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film 50, and the ratio of P-TEOS silicon oxide in the intermediary film 56. The intermediary layer film 56 is an intermixed film that is formed on the interface between the P-TEOS silicon oxide film 52 and the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film 50. The thickness is measured after the formation of the multi layered film.

0077 – As in the table 3, when the TEOS silicon oxide film 54 and the P-TEOS silicon oxide film 52 are formed on the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film 50 under the above conditions, the quality of the film 50 barely changes therefore, its optical requirements remain unchanged.

0078 – Also, as shown in the chart 19, the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film 50 as a reflection preventive film, the P-TEOS silicon oxide film 52 and the LP-TEOS silicon oxide film 54 are formed on the tungsten silicide substrate 48. A curved line B shows the Standing Wave Effects after putting the resist film over the films 50, 52 and 54. A curved line B in the chart 20 shows the Standing Wave Effects when the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film 50 as a reflection preventive film is not formed. It is confirmed that the effect declines.

0079 – In the experiment shown in the chart 20, KrF with wave length  $\lambda$  is 248 nm is used as exposure light and XP8843 is used as a resist film. The assumption figures of n and k are as follows:

	k	n
resist film	1.80 ( $n_{pr}$ )	0.011( $k_{pr}$ )
tungsten silicide	1.93	2.73.
$\text{Si}_x\text{O}_y\text{N}_z : \text{H}$ film 50	2.12	0.54.
LP-TEOS silicon oxide/P-TEOS silicon oxide film	1.52	0

0080 – Example 3

In this example, the semiconductor device is manufactured in the same way as shown in the example

1, except that the constitutions of the offset oxide film is layer-built film with a protective film and an intermediately interlayer film.

0081 – A protective film has thickness of 20-100 nm and is constituted by a silicon oxide film, which is formed by CVD method at below 500 C, and a silicon oxide film, which is formed by the ozone TEOS method. It is desired that the interlayer film is an inorganic film with 80-200 nm thickness and its optical constant is same as the protective film's. The interlayer film is constituted by a silicon oxide film which is formed by the LP-TEOS method.

#### 0082 – Example 4

In this example, the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film as a reflection protective film is formed by the following method. Other than this, the semiconductor device is manufactured the same way as example 1 through 3.

0083 – In this example, the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film is formed using the parallel flat style plasma CVD method, ECR plasma CVD method, or bias ECR plasma CVD method with micro wave of 2.45 GHz and mixed gas of  $\text{SiH}_4 + \text{N}_2$  or  $\text{SiH}_4 + \text{O}_2 + \text{N}_2$ .

#### 0084 - Example 5

In this example, the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film as a reflection protective film is formed by the following method. Other than this, the semiconductor device is manufactured the same way as example 1 through 3.

0085 – In this example, the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film is formed using the parallel flat style plasma CVD method, ECR plasma CVD method, or bias ECR plasma CVD method with micro wave of 2.45 GHz and mixed gas of  $\text{SiH}_4 + \text{N}_2$  or  $\text{SiH}_4 + \text{O}_2 + \text{N}_2$ . The Ar is used as buffer gas.

#### 0086 - Example 6

In this example, the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film as a reflection protective film is formed by the following method. Other than this, the semiconductor device is manufactured in the same way as examples 1 through 3.

0087 – In this example, the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film is formed using the parallel flat style plasma CVD method, the ECR plasma CVD method, or the bias ECR plasma CVD method with micro wave of 2.45 GHz and mixed gas of  $\text{SiH}_4 + \text{N}_2$  or  $\text{SiH}_4 + \text{O}_2 + \text{N}_2$ .

#### 0088 – Example 7

In this example, the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film as a reflection protective film is formed by the following method. Other than this, the semiconductor device is manufactured in the same way as examples 1 through 3.

0089 – In this example, the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film is formed using the parallel flat style plasma CVD method, the ECR plasma CVD method, or the bias ECR plasma CVD method with micro wave of 2.45 GHz and mixed gas of  $\text{SiH}_4 + \text{N}_2$  or  $\text{SiH}_4 + \text{O}_2 + \text{N}_2$ .

#### 0090 – Example 8

In this example,  $\text{Si}_x\text{N}_y$  is used as a reflection protective film instead of the  $\text{Si}_x\text{O}_y\text{N}_z : \text{H}$  film shown in the examples 1 through 3, and is formed by the following method. Other than this, the semiconductor device is manufactured in the same way as examples 1 through 3.

0091 – In this example, the reflection preventive film is formed using the parallel flat style plasma CVD method, the ECR plasma CVD method, or the bias ECR plasma CVD method with micro wave of 2.45 GHz and mixed gas of  $\text{SiH}_4 + \text{NH}_3$  or  $\text{SiH}_2\text{Cl}_2 + \text{NH}_3$ .

#### 0092 – Example 9

In this example,  $\text{Si}_x\text{N}_y$  is used as a reflection protective film instead of the  $\text{Si}_x\text{O}_y\text{N}_z:\text{H}$  film shown in the examples 1 through 3, and is formed by the following method. Other than this, the semiconductor device is manufactured in the same way as examples 1 through 3.

0093 – In this example, the reflection preventive film is formed using the parallel flat style plasma CVD method, the ECR plasma CVD method, or the bias ECR plasma CVD method with micro wave of 2.45 GHz and mixed gas of  $\text{SiH}_4 + \text{O}_2$  or  $\text{SiH}_2\text{Cl}_2 + \text{NH}_3$ . The Ar is used as buffer gas.

#### 0094 – Example 10

In this example,  $\text{Si}_x\text{N}_y$  is used as a reflection protective film instead of the  $\text{Si}_x\text{O}_y\text{N}_z:\text{H}$  film shown in the examples 1 through 3, and is formed by the following method. Other than this, the semiconductor device is manufactured in the same way as examples 1 through 3.

0095 – In this example, a reflection preventive film is formed using the parallel flat style plasma CVD method, the ECR plasma CVD method, or the bias ECR plasma CVD method with micro wave of 2.45 GHz and mixed gas of  $\text{SiH}_4 + \text{O}_2$  or  $\text{SiH}_2\text{Cl}_2 + \text{NH}_3$ .

#### 0096 – Example 11

In this example,  $\text{Si}_x\text{N}_y$  is used as a reflection protective film instead of the  $\text{Si}_x\text{O}_y\text{N}_z:\text{H}$  film shown in the examples 1 through 3, and is formed by the following method. Other than this, the fine pattern is formed to the semiconductor device in the same way as examples 1 through 3.

0097 – In this example, a reflection preventive film is formed using the parallel flat style plasma CVD method, the ECR plasma CVD method, or the bias ECR plasma CVD method with micro wave of 2.45 GHz and mixed gas of  $\text{SiH}_4 + \text{O}_2$  or  $\text{SiH}_2\text{Cl}_2 + \text{NH}_3$ . The Ar is used as buffer gas.

#### 0098 – Effect

With this semiconductor manufacturing method, in the process of producing the semiconductor device using a 365 nm of i-line or longer than of its wavelength light, i-line or KrF, ArF Excimer laser, as a light source, it is possible to form a stable fine pattern by forming a protective film on the reflection preventive film even though the reflection preventive film has stoichiometrically unstable bonds.

0099 – That means that using an inorganic film which has both reflection preventive effect and inorganic mask function it is possible to form a stable mask pattern on the wiring layers without increasing manufacturing process even though the semiconductor mask pattern is fine and has level structure. The  $\text{Si}_x\text{O}_y\text{N}_z:\text{H}$  film is the most appropriate inorganic film.

#### Explanation of the chart:

Chart 1 – the outline of the light interference in the resist film

Chart 2 – the Standing Wave Effects on the silicon substrate

Chart 3 – assumption of influence to the Standing Wave Effects by level difference

Chart 4 – relationship between fluctuations of light absorption and pattern size

Chart 5 - the Standing Wave Effects on the silicon substrate

Chart 6 – contour of light absorption when optical constants, n and k are variables while the thickness of the reflection preventive film is fixed.

Chart 7 – different thickness of the resist films shows the same contour of the light absorption in the chart 6

- Chart 8 - different thickness of the resist films shows the same contour of the light absorption in the chart 6
- Chart 9 - different thickness of the resist films shows the same contour of the light absorption in the chart 6
- Chart 10 – A and B shows the changes of optical constants of  $\text{Si}_x\text{O}_y\text{N}_z$  when manufacturing conditions change
- Chart 11 – reflection preventive effect when the  $\text{Si}_x\text{O}_y\text{N}_z$ : H film is formed on the tungsten silicide substrate
- Chart 12 - reflection preventive effect when the  $\text{Si}_x\text{O}_y\text{N}_z$ : H film is formed on the aluminum silicon silicide substrate
- Chart 13 - reflection preventive effect when the  $\text{Si}_x\text{O}_y\text{N}_z$ : H film is formed on the silicon substrate
- Chart 14 – analysis of FT-IR spectrum when the  $\text{Si}_x\text{O}_y\text{N}_z$ : H film is annealed.
- Chart 15 – a sectioned diagram of manufacturing process of this semiconductor device
- Chart 16 – outline of experiment of protective film effect
- Chart 17 – outline sectioned diagram of manufacturing process of this semiconductor device
- Chart 18 – continuation of chart 17
- Chart 19 – outline of experiment of protective film effect
- Chart 20 – Standing Wave Effects when reflection preventive film and protective film are layered

Code:

- 2 – semiconductor substrate
- 4 – element isolation region
- 6 – gate insulation film
- 8 – poly silicon film
- 10 – tungsten silicide film
- 12 – reflection protective film
- 14 – protective film (offset oxide film)
- 30 – first wiring layer
- 32 – second wiring layer
- 34 – contact hole
- 36 – first interlayer insulation film
- 38 – reflection protective film
- 40 – protective film
- 42 – second interlayer insulation film
- 44 – resist film